

Supporting Information

Dynamic Induction of Enantiomeric Excess from a Prochiral Azobenzene Dimer Under Circularly Polarized Light

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1. General experimental methods.

All solvents and chemicals were obtained from commercial sources and used without further purification, unless otherwise stated. ^1H and ^{13}C NMR spectra were recorded using a JEOL ECX 400 spectrometer, with tetramethylsilane as the internal standard. Electrospray ionization (ESI⁺) mass spectrometry was performed using an AccuTOF instrument (JMS-T100LC; JEOL). X-ray crystallographic data were acquired using a Bruker Smart Apex diffractometer. Absorption spectra were recorded using an Agilent 8453 spectrophotometer. CD spectra were recorded using a JASCO J-720 spectrophotometer; baseline correction and binomial smoothing were applied to the spectra. Photoisomerization studies were conducted using radiation from an LED source of 365 nm and a super-high-pressure mercury lamp (500 W, Ushio) after passage through 436-nm filters. High-performance liquid chromatography (HPLC) was performed using a Hitachi Elite La Chrome HPLC system and a Chiralpak IA column (Daicel Chemical Industries). Compositions of photostationary states were determined through HPLC analysis. A mixture of isopropanol and hexane (1:4) was used as the eluent in the HPLC experiments.

2. Synthesis

Compound 4: A mixture of 1-chloro-2,6-dinitrobenzene (250 mg, 1.23 mmol), iodonaphthalene (320 mg, 1.26 mmol), and copper bronze (320 mg, 5.04 mmol) was heated at 120 °C for 12 h (until the spot for dinitrochlorobenzene disappeared in TLC analysis). The product was extracted into CH₂Cl₂; the combined extracts were washed with water and dried (MgSO₄). The solvent was evaporated under vacuum and the residue subjected to column chromatography (SiO₂; CH₂Cl₂/hexane, 2:3) to give a pale yellow solid (38% yield). ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS); δ = 8.16 (d, *J*=8.2 Hz, 2H), 7.92 (dd, *J*=8.2, 8.3, 2H), 7.81 (t, *J*=8.2 Hz, 1H), 7.49–7.53 (m, 2H), 7.42–7.46 (m, 1 H), 7.33–7.34 (m, 2H).

Compound 5: Compound 4 (100 mg, 0.34 mmol) was dissolved in a 2:1 mixture of EtOH and 1,4-dioxane (5 mL) and then the reaction flask was evacuated and backfilled with Ar three times. PtO₂ (10 mg, 0.4 mmol) was added under an Ar atmosphere and then the atmosphere was changed from Ar to H₂. The reaction mixture was stirred at room temperature until TLC (mobile phase: 20% EtOAc/hexane) revealed a single spot, approximately overnight. The catalyst was removed by filtration over Celite; the solvent was evaporated to dryness under vacuum to yield a brownish solid (71 mg, 90% yield). ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ = 7.90–7.92 (m, 2H), 7.67 (d, *J*=8.5 Hz, 1H), 7.58–7.61 (m, 1H), 7.49–7.54 (m, 2H), 7.42–7.46 (m, 1H), 7.07 (t, *J*=7.9 Hz, 1H), 3.32 (s, 4H); MS (ESI⁺): calcd for C₁₆H₁₄N₂ [M + H]⁺: *m/z* 235.12; found: 235.11.

3. NMR spectra

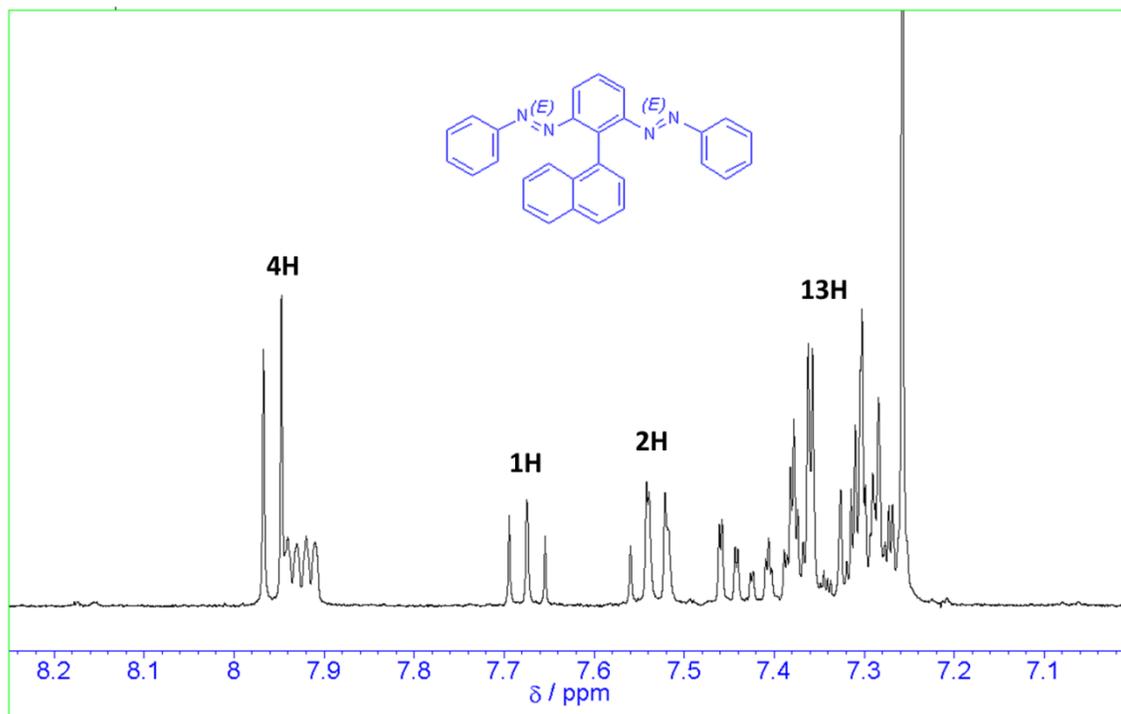


Figure S1. ¹H NMR spectrum of compound **3** in CDCl₃ at room temperature.

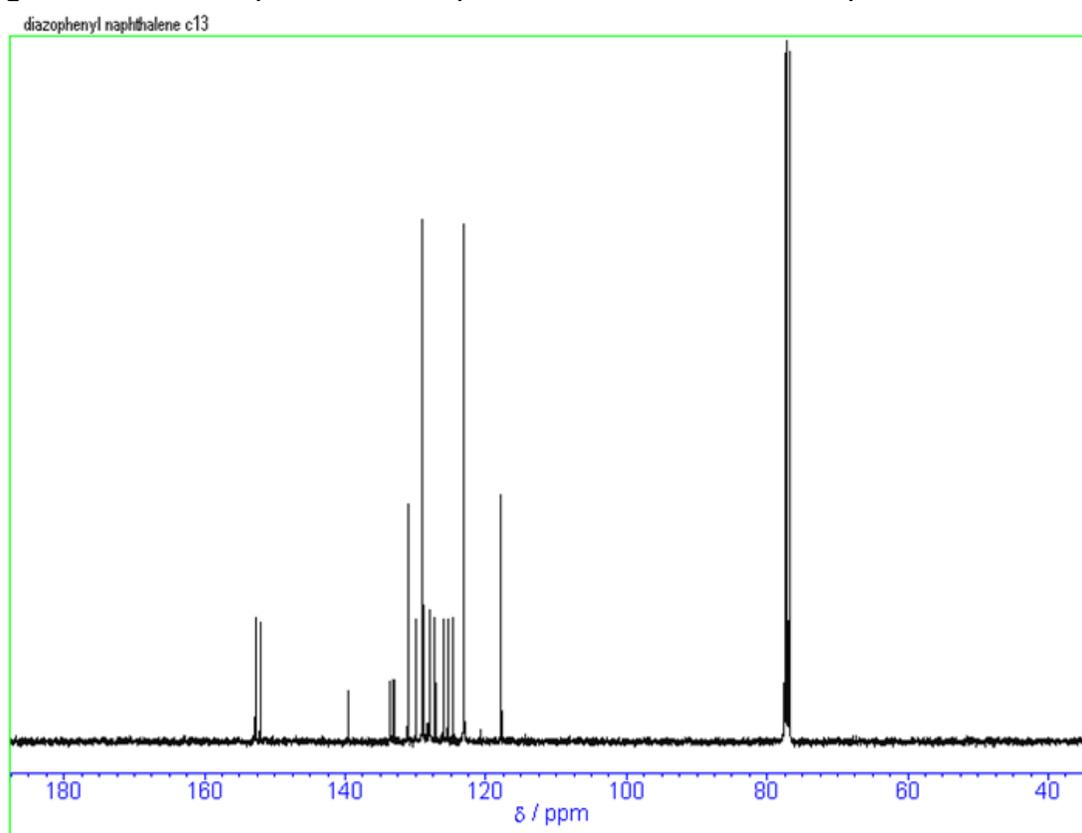


Figure S2. ¹³C NMR spectrum of compound **3** in CDCl₃ at room temperature.

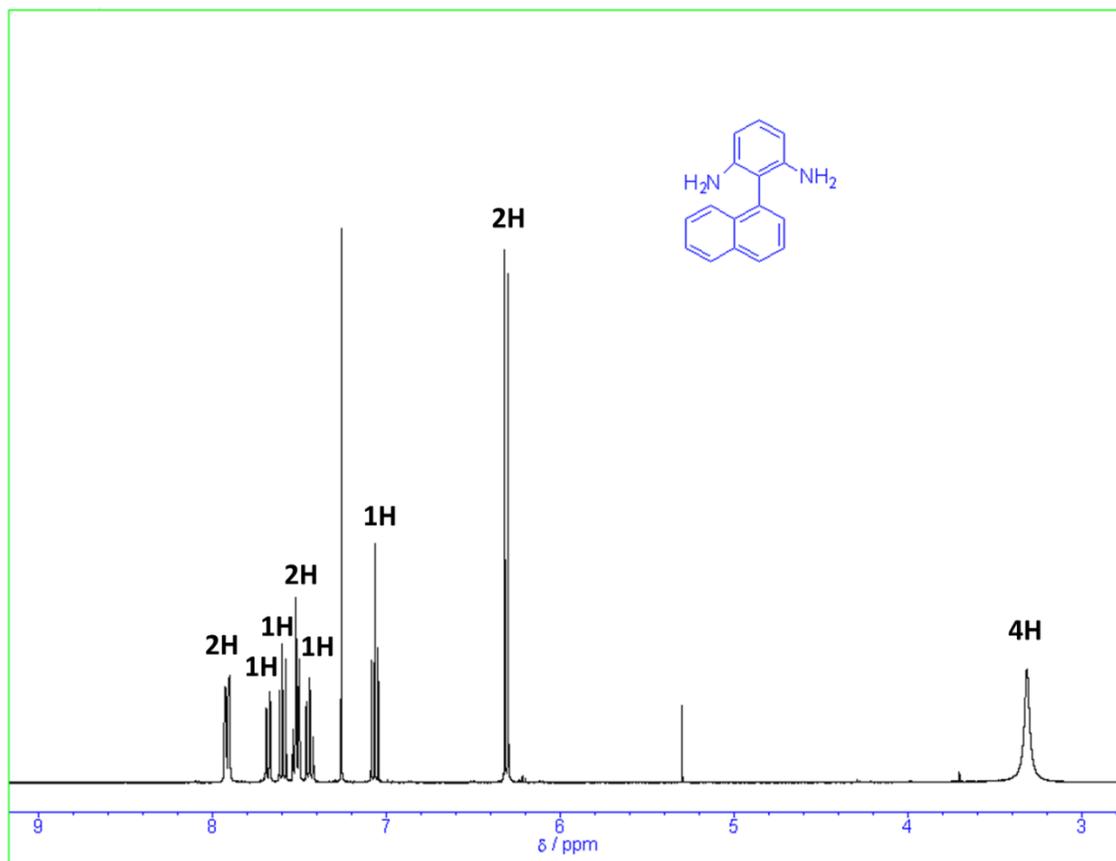


Figure S3. ¹H NMR spectrum of compound **5** in CDCl₃ at room temperature

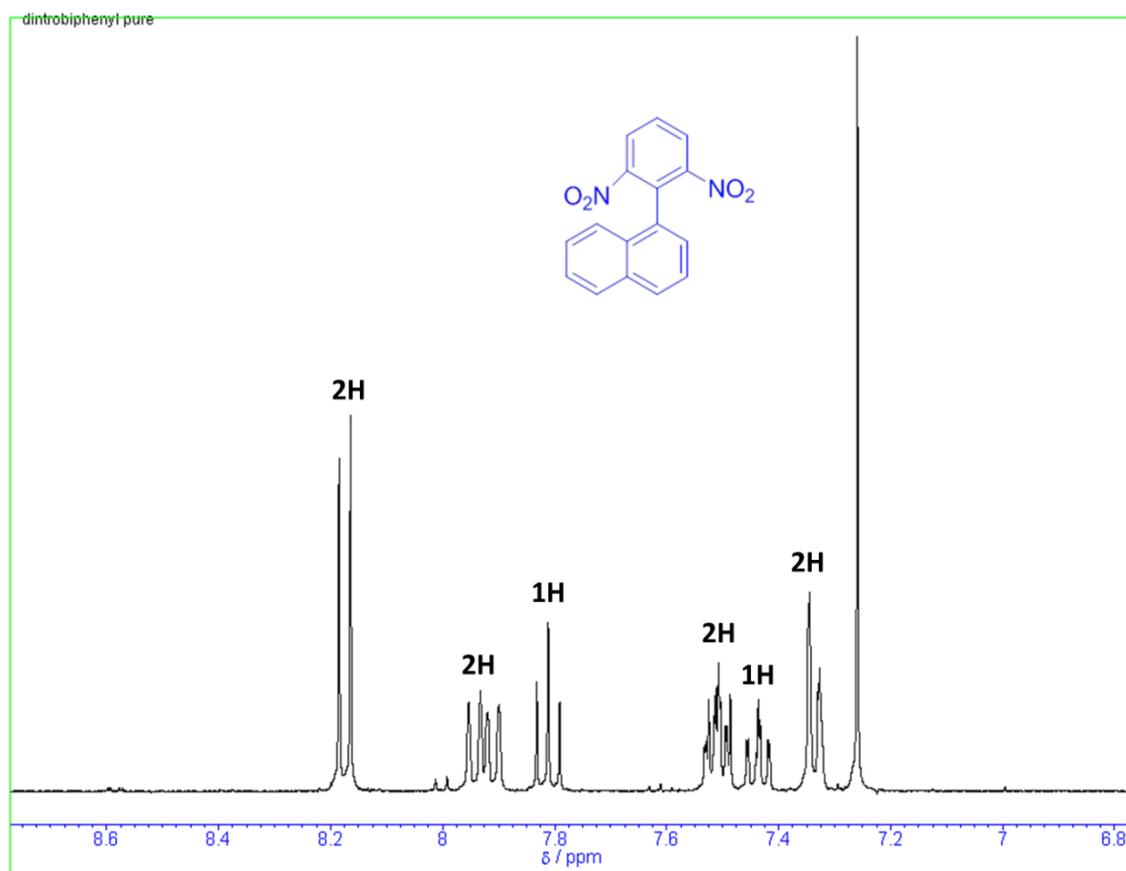


Figure S4. ¹H NMR spectrum of compound **4** in CDCl₃ at room temperature.

4. UV-Vis absorption spectra

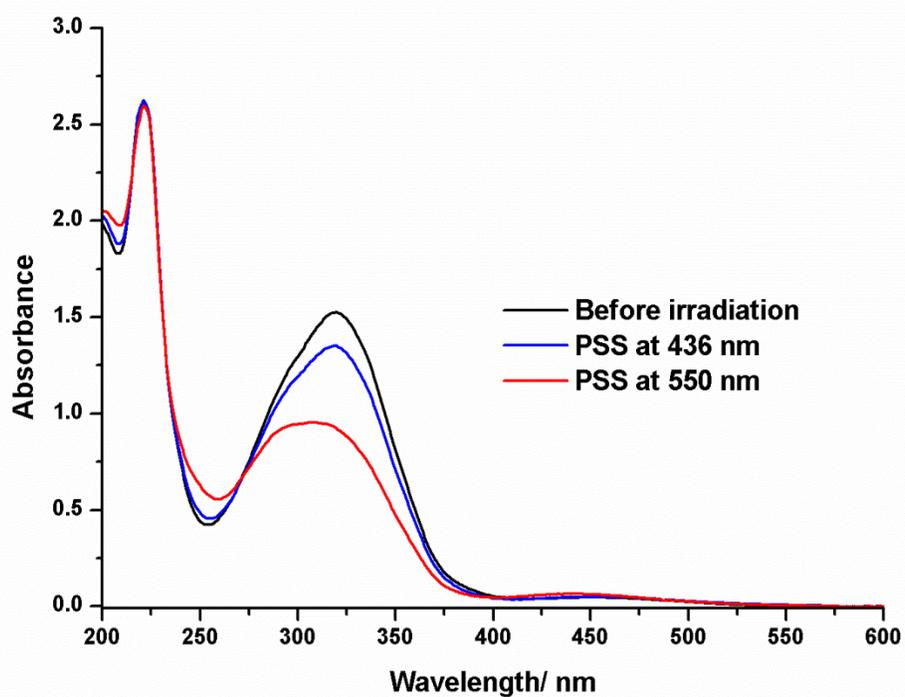


Figure S5. Visible light switching of **3** in MeCN at room temperature.

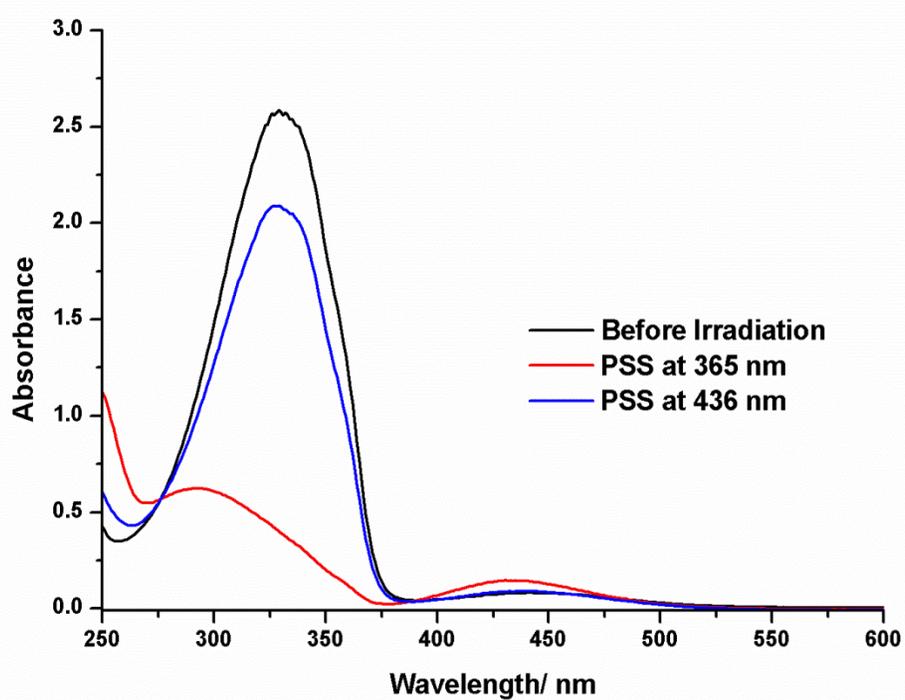


Figure S6. Absorption spectra of compound **1** in MeCN (5.1×10^{-4} M) before and after irradiation at 365 and 436 nm.

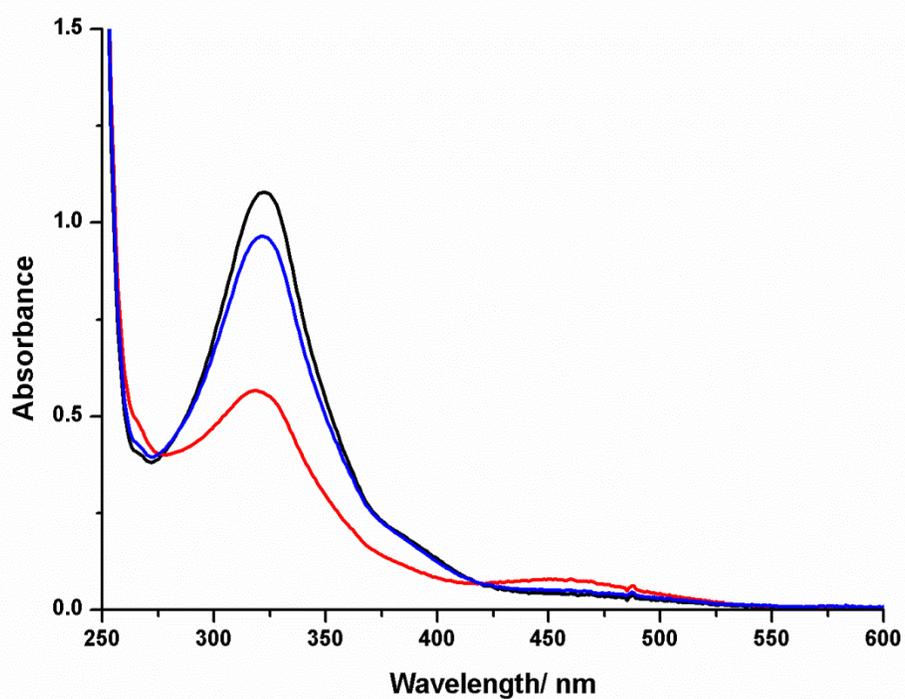


Figure S7. Absorption spectra of compound **2** in MeCN (3.69×10^{-4} M) before (black line) and after irradiation at 365 (red line) and 436 (blue line) nm.

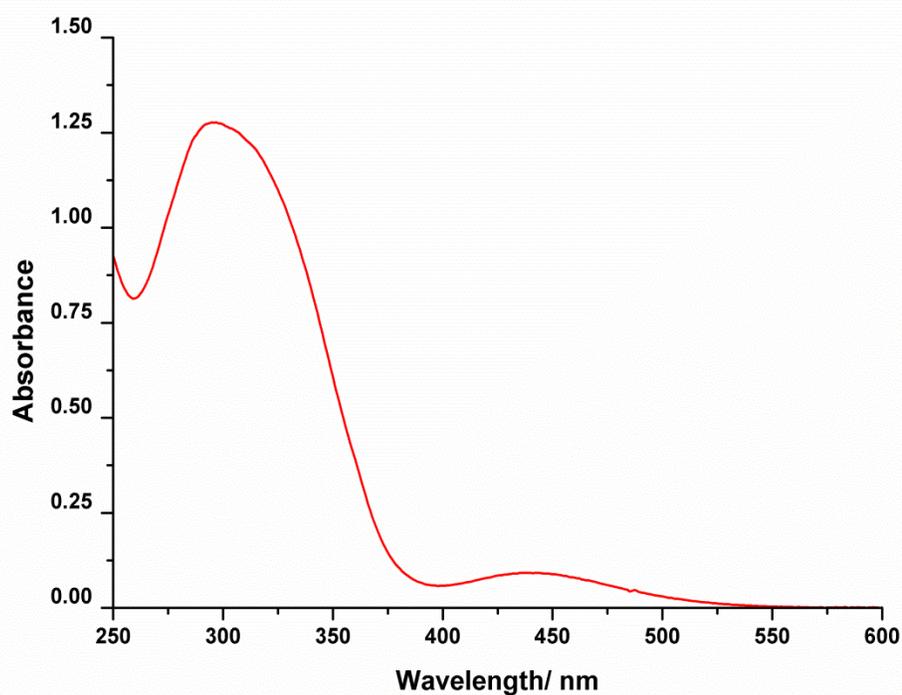


Figure S8. Absorption spectrum of *EZ-3_A* in MeCN after HPLC separation. An identical spectrum was obtained for *EZ-3_B*.

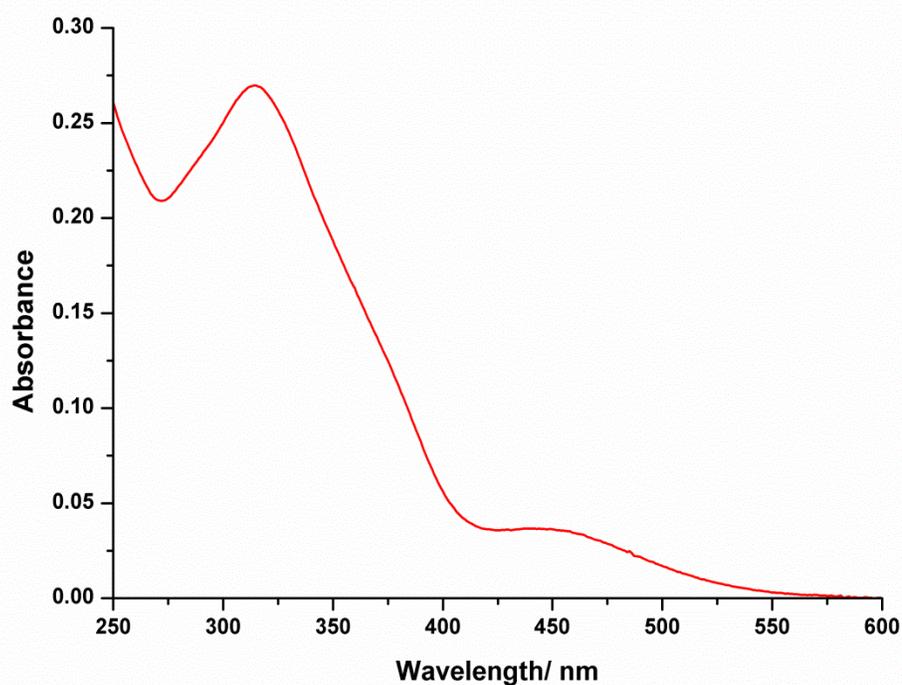


Figure S9. Absorption spectrum of *EZ-2_A* in MeCN after HPLC separation. An identical spectrum was obtained for *EZ-2_B*.

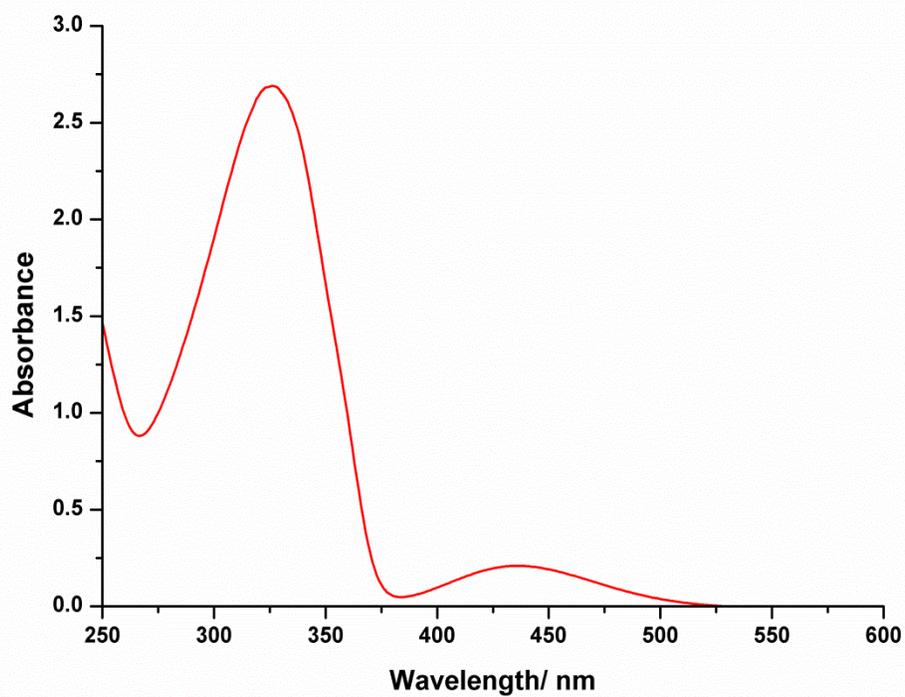


Figure S10. Absorption spectrum of *EZ-1_A* in MeCN after HPLC separation. An identical spectrum was obtained for *EZ-1_B*.

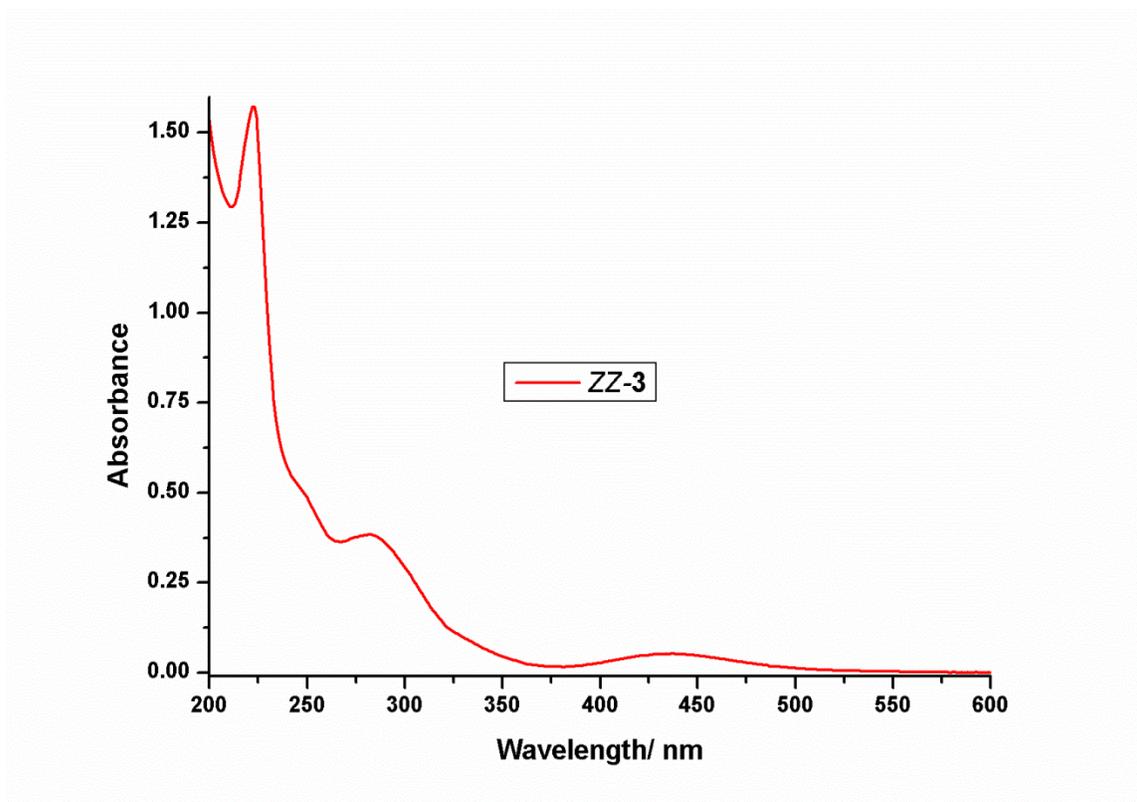


Figure S11. Absorption spectrum of ZZ-3 in MeCN after HPLC separation.

5. HPLC Chromatogram

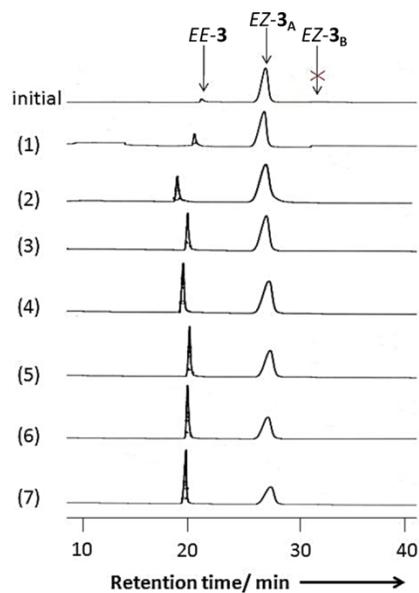


Figure S12. HPLC profile revealing the absence of racemization during the thermal back-isomerization of *EZ-3_A*, the first-eluted enantiomer of *EZ-3*, in the dark at room temperature over one week.

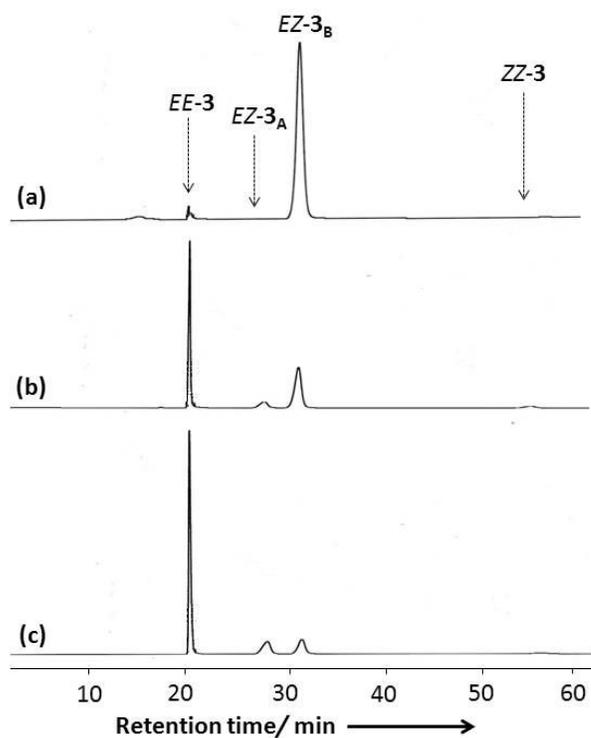


Figure S13. HPLC chromatograms of *EZ-3_B*, the second-eluted enantiomer of *EZ-3*: (a) before irradiation, (b) after irradiation for 10 s at 436 nm, and (c) the PSS at 436 nm.

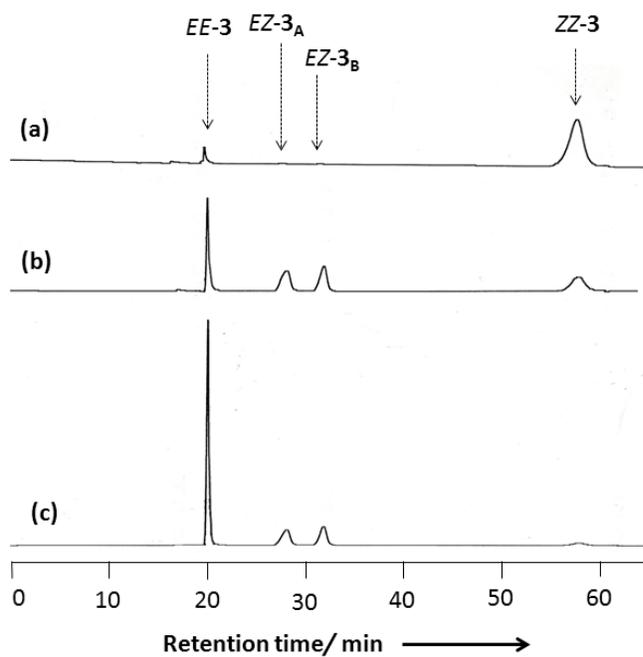


Figure S14. HPLC chromatograms revealing the *ZZ*-to-*EE* photoisomerization pathway of compound **3** via the *EZ* intermediate: (a) before irradiation, (b) after irradiation for 10 s at 436 nm, and (c) the PSS at 436 nm.

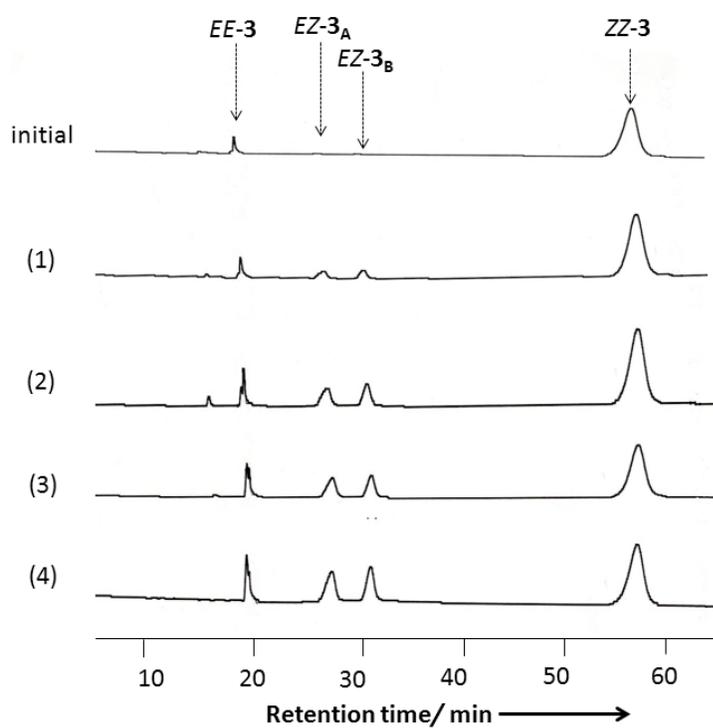


Figure S15. HPLC chromatograms revealing the *ZZ*-to-*EE* thermal isomerization of compound **3** via the *EZ* intermediate, in the dark at room temperature.

6. CD Spectra

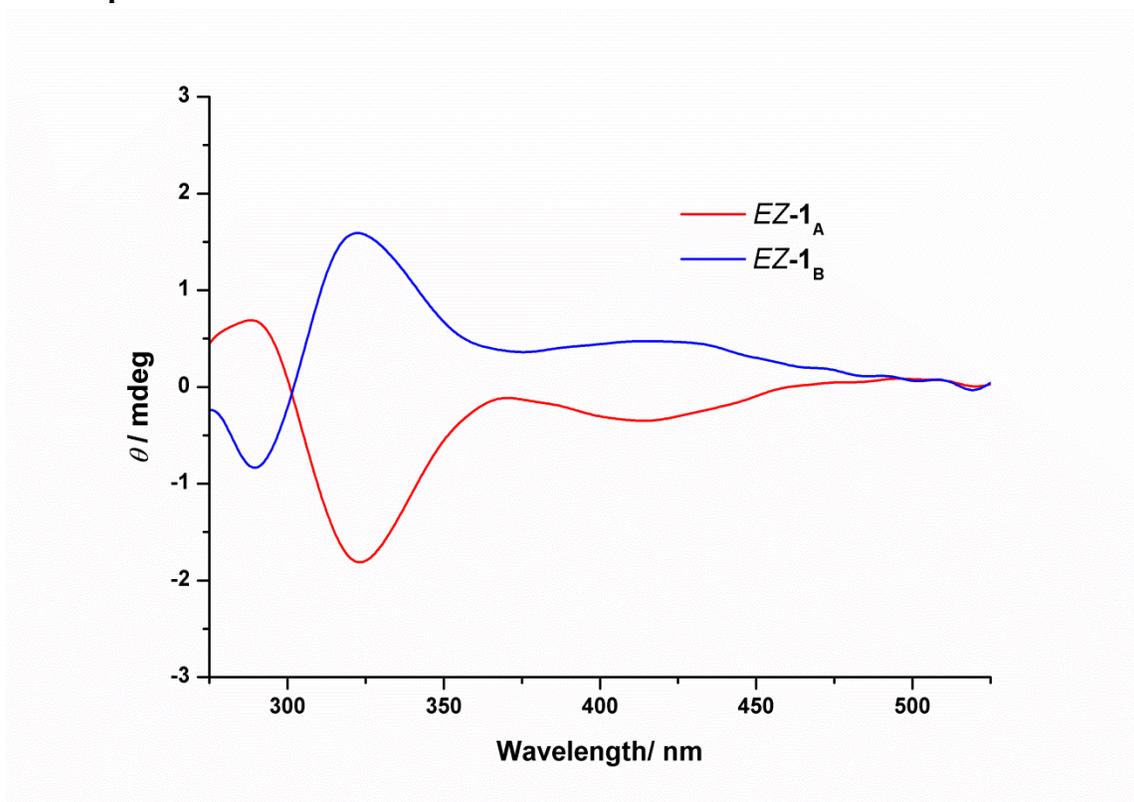


Figure S16. CD spectra of *EZ-1* in MeCN; (red line) first-eluted enantiomer, *EZ-1*_A; (blue line) second-eluted enantiomer, *EZ-1*_B. Concentration of each solution: 1.01×10^{-4} M.

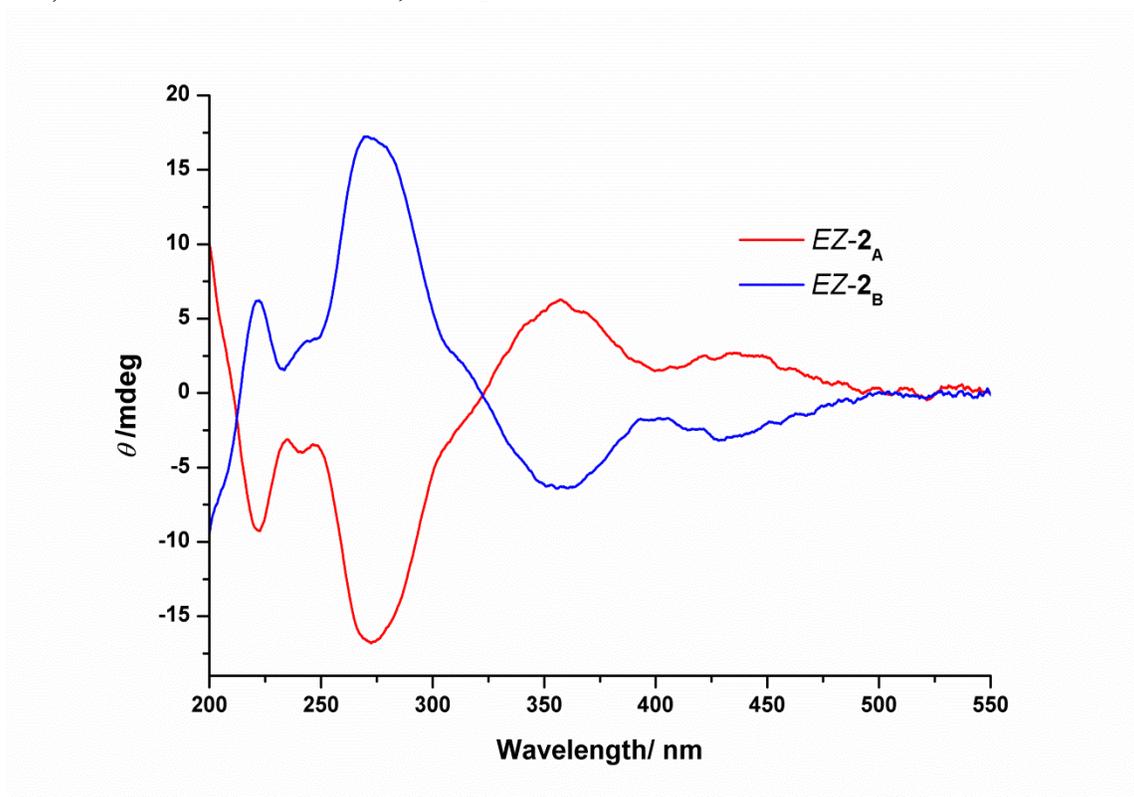


Figure S17. CD spectra of *EZ-2* in MeCN; (red line) first-eluted enantiomer, *EZ-2*_A; (blue line) second-eluted enantiomer, *EZ-2*_B. Concentration of each solution: 1.94×10^{-4} M.

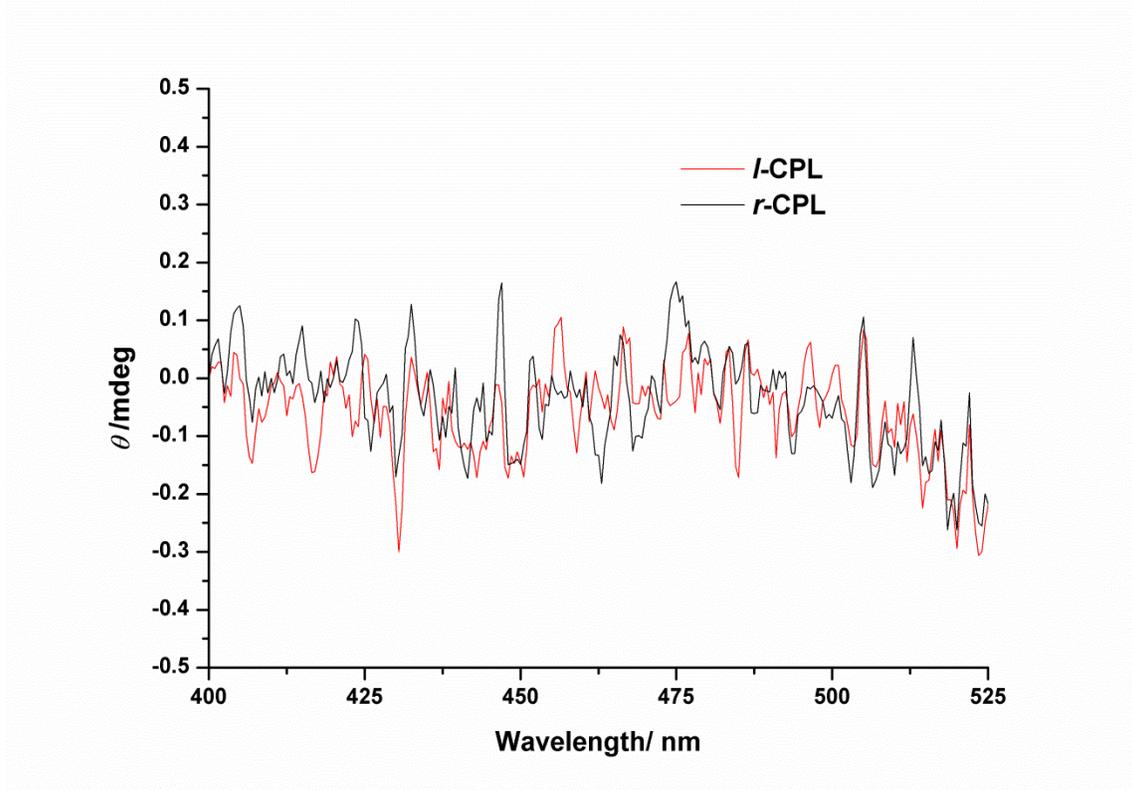


Figure S18. CD spectra of a solution of **1** (1.42×10^{-3} M) in MeCN after irradiation with *r*-CPL (black line) and *l*-CPL (red line), revealing no induced CD at PSS₄₃₆.

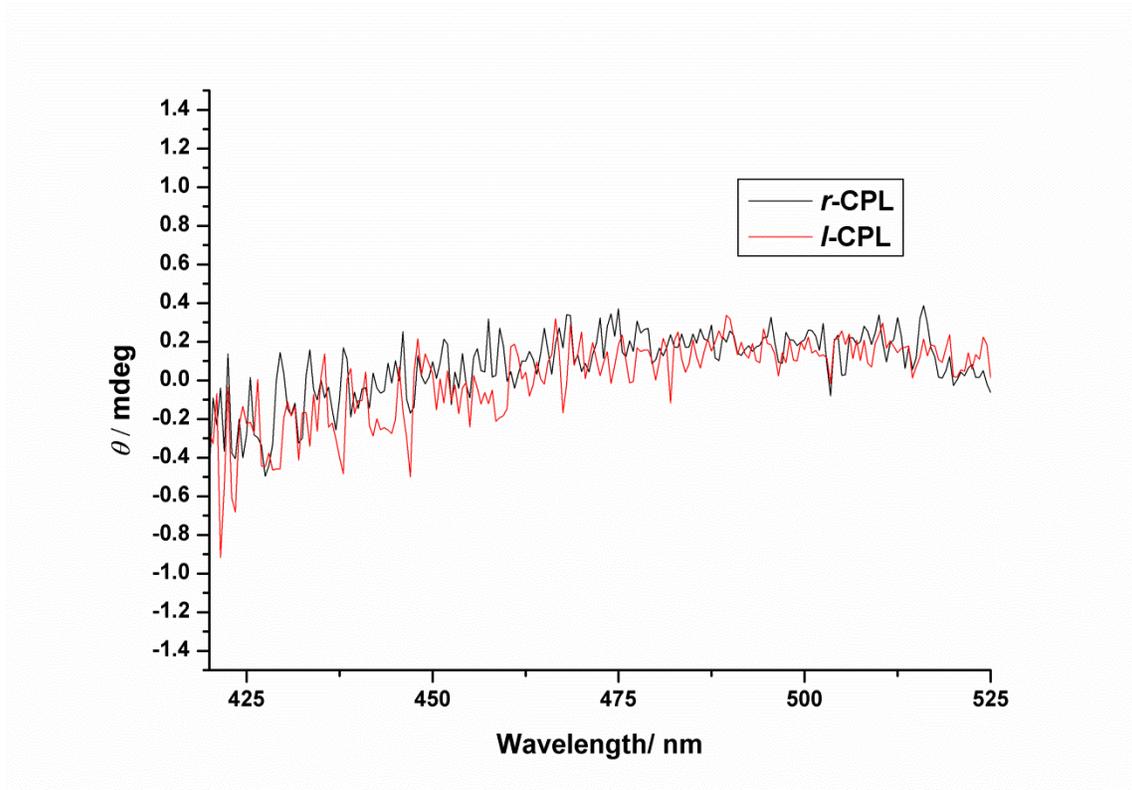


Figure S19. CD spectra of a solution of **2** (1.5×10^{-3} M) in MeCN after irradiation with *r*-CPL (black line) and *l*-CPL (red line), revealing no induced CD at PSS₄₃₆.

7. Kinetic studies

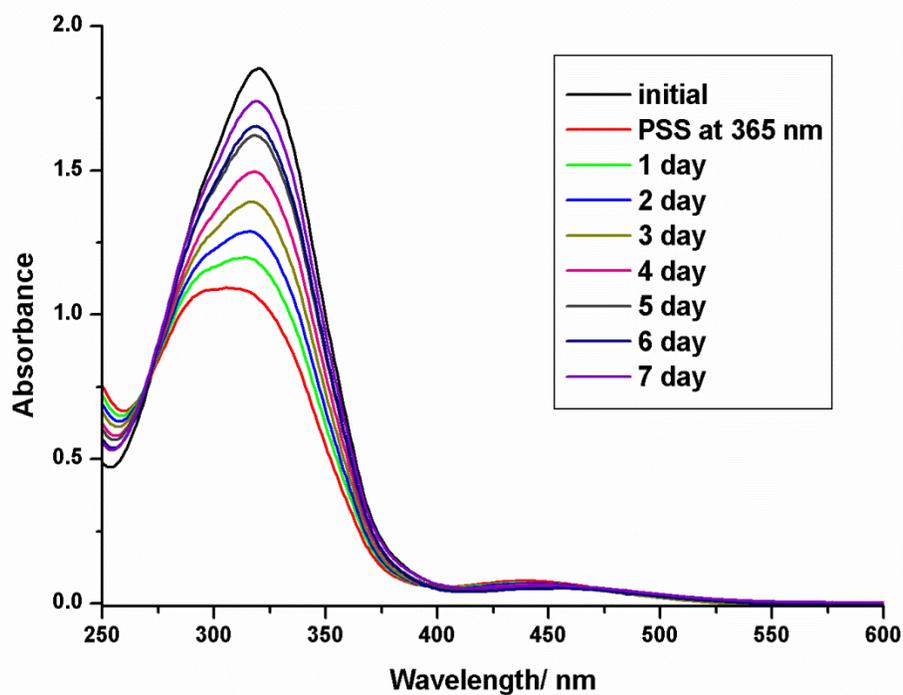


Figure S20. UV spectra of a solution of **3** (1.5×10^{-3} M) in MeCN during thermal back-isomerization after PSS_{365 nm}, at 30 °C in the dark for 7 days.

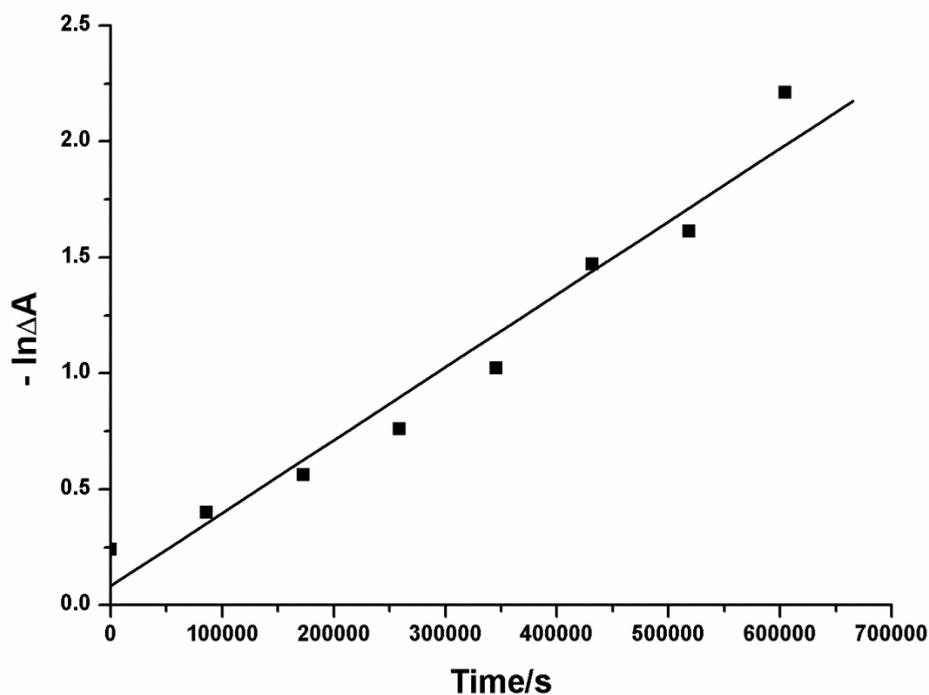


Figure S21. Linear relationship between the logarithm of the change in absorbance ($\Delta A = A_i - A_t$, determined from the absorbance at 320 nm in the UV spectra, where A_i is the initial absorbance before irradiation and A_t is the absorbance at time t after PSS_{366 nm}) and time for **3** after PSS_{365 nm} at 30 °C.

8. Estimation of the enantiomeric excess after CPL irradiation

The enantiomeric excess in the photoresolution process is estimated by the following calculation,

The photochemical rate equations in a 1cm cell are

$$\frac{d[R-EZ]}{dt} = 1000I_0 \{(1-10^{-A})/A\} \{(\epsilon_{EE} \phi_{EE \rightarrow EZ} [EE] + \epsilon_{ZZ} \phi_{ZZ \rightarrow EZ} [ZZ]) - (\epsilon_{R-EZ} \phi_{R-EZ \rightarrow EE} [R-EZ] + \epsilon_{R-EZ} \phi_{R-EZ \rightarrow ZZ} [R-EZ])\} \quad (1)$$

$$\frac{d[S-EZ]}{dt} = 1000I_0 \{(1-10^{-A})/A\} \{(\epsilon_{EE} \phi_{EE \rightarrow EZ} [EE] + \epsilon_{ZZ} \phi_{ZZ \rightarrow EZ} [ZZ]) - (\epsilon_{S-EZ} \phi_{S-EZ \rightarrow EE} [S-EZ] + \epsilon_{S-EZ} \phi_{S-EZ \rightarrow ZZ} [S-EZ])\} \quad (2)$$

where $[R-EZ]$, $[S-EZ]$, $[EE]$, $[ZZ]$ and ϵ_{R-EZ} , ϵ_{S-EZ} , ϵ_{EE} , ϵ_{ZZ} are concentrations and molar extinction coefficients of $R-EZ$, $S-EZ$, EE , ZZ isomers, respectively, and $\phi_{EE \rightarrow EZ}$, $\phi_{ZZ \rightarrow EZ}$, $\phi_{EZ \rightarrow EE}$, $\phi_{EZ \rightarrow ZZ}$ represents the quantum yields of photochemical isomerization from $EE \rightarrow EZ$, $ZZ \rightarrow EZ$, $EZ \rightarrow EE$, $EZ \rightarrow ZZ$, respectively.

At the photostationary state,

$$\frac{d[R-EZ]}{dt} = \frac{d[S-EZ]}{dt} = 0 \quad (3)$$

Then,

$$\epsilon_{EE} \phi_{EE \rightarrow EZ} [EE] + \epsilon_{ZZ} \phi_{ZZ \rightarrow EZ} [ZZ] = \epsilon_{R-EZ} \phi_{R-EZ \rightarrow EE} [R-EZ] + \epsilon_{R-EZ} \phi_{R-EZ \rightarrow ZZ} [R-EZ] \quad (4)$$

$$\epsilon_{EE} \phi_{EE \rightarrow EZ} [EE] + \epsilon_{ZZ} \phi_{ZZ \rightarrow EZ} [ZZ] = \epsilon_{S-EZ} \phi_{S-EZ \rightarrow EE} [S-EZ] + \epsilon_{S-EZ} \phi_{S-EZ \rightarrow ZZ} [S-EZ] \quad (5)$$

Equating 4 and 5,

$$\epsilon_{R-EZ} \phi_{R-EZ \rightarrow EE} [R-EZ] + \epsilon_{R-EZ} \phi_{R-EZ \rightarrow ZZ} [R-EZ] = \epsilon_{S-EZ} \phi_{S-EZ \rightarrow EE} [S-EZ] + \epsilon_{S-EZ} \phi_{S-EZ \rightarrow ZZ} [S-EZ] \quad (6)$$

$$\epsilon_{R-EZ} [R-EZ] (\phi_{R-EZ \rightarrow EE} + \phi_{R-EZ \rightarrow ZZ}) = \epsilon_{S-EZ} [S-EZ] (\phi_{S-EZ \rightarrow EE} + \phi_{S-EZ \rightarrow ZZ}) \quad (7)$$

Since $R-EZ$ and $S-EZ$ enantiomers are chemically same, the interconversion quantum yields must be identical for symmetry reasons.

Therefore equation 7 can be written as

$$\epsilon_{R-EZ} [R-EZ] = \epsilon_{S-EZ} [S-EZ] \quad (8)$$

This leads, as $\epsilon_{R-EZ} = \epsilon_{EZ} - (\Delta\epsilon_{EZ}/2)$ and $\epsilon_{S-EZ} = \epsilon_{EZ} + (\Delta\epsilon_{EZ}/2)$, to

$$\{\epsilon_{EZ} - (\Delta\epsilon_{EZ}/2)\} [R-EZ] = \{\epsilon_{EZ} + (\Delta\epsilon_{EZ}/2)\} [S-EZ] \quad (9)$$

Then, equation 9 can be deduced to,

$$\epsilon_{EZ} \{ [R-EZ] - [S-EZ] \} = (\Delta\epsilon_{EZ}/2) \{ [R-EZ] + [S-EZ] \} \quad (10)$$

$$([R-EZ] - [S-EZ]) / ([R-EZ] + [S-EZ]) = \Delta\epsilon_{EZ} / 2\epsilon_{EZ} \quad (11)$$

Kuhn anisotropy factor, g is defined as,

$$g = \Delta\epsilon / \epsilon \quad (12)$$

from the equations 11 and 12, equation 13 can be obtained,

$$([R-EZ] - [S-EZ]) / ([R-EZ] + [S-EZ]) = g_{EZ} / 2 \quad (13)$$

Table S1. Crystallographic data of **3**.

	3
Formula	C ₂₈ H ₂₀ N ₄
Formula weight	412.49
Crystal system	Triclinic
Space group	<i>P</i> 1–
<i>a</i> / Å	7.8497(5)
<i>b</i> / Å	10.7861(8)
<i>c</i> / Å	14.7876(10)
α / °	109.560(3)
β / °	91.8983(18)
γ / °	111.312(3)
<i>V</i> / Å ³	1081.88(13)
<i>Z</i>	2
Crystal size / mm	0.50 × 0.30 × 0.30
<i>T</i> / K	173
<i>D</i> _c / g cm ⁻³	1.266
<i>F</i> ₀₀₀	432.00
λ / Å	0.71075
μ (Mo-K α) / cm ⁻¹	0.763
Data measured	10582
Data unique	4868
<i>R</i> _{int}	0.0242
No. of observations	4868
No. of variables	289
<i>R</i> ₁ (<i>I</i> > 2.00 σ (<i>I</i>)) ^a	0.0503
<i>R</i> (all reflections) ^a	0.0597
<i>wR</i> ₂ (all reflections) ^b	0.1454
GOF	1.065
CCDC number	1003754

^a $R_1 = R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$. ^b $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{1/2}$.